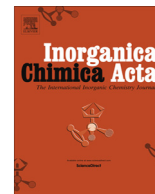




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Research paper

## Counterion effect on the spin-transition properties of the second generation iron(III) dendrimeric complexes

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## ABSTRACT

The magnetic properties and the influence of counterions on the spin crossover properties of two novel Fe(III) dendrimeric complexes of the second generation, namely  $[\text{Fe}(\text{L})_2]^+\text{X}^-$ , where  $\text{L} = 3,5\text{-di}(3,4,5\text{-tris(tetradecyloxy)benzoyloxy)benzoyl-4-oxy-salicylidene-N'-ethyl-N-ethylenediamine}$   $\text{X} = \text{Cl}^-$  (**1**),  $\text{ClO}_4^-$  (**2**), have been studied for the first time by magnetic susceptibility measurements and electron paramagnetic resonance (EPR) method in a wide (4.2–300 K) temperature range. EPR results showed that compound **1** contains about 98% of high-spin (HS,  $S = 5/2$ ) and ~2% of low-spin (LS,  $S = 1/2$ ) Fe(III) centers, and undergoes an antiferromagnetic ordering below 7 K. The EPR integrated intensity of a broad line ( $g \approx 2$ ), corresponding to the HS iron(III) centers, passes through a broad maximum at  $T_{\text{max}} \approx 100$  K, which is indicative of short-range correlation effects. The anomalous broadening of this EPR line at low temperatures with the critical exponent  $\beta = 1.5$  upon approaching the long-range ordering transition ( $T_{\text{N}}^{\text{EPR}} = 7$  K) from above indicates the quasi-two-dimensional antiferromagnetic nature of magnetism in complex **1**. The spin-crossover effect is completely suppressed in compound **1**. The complex with  $\text{ClO}_4^-$  counterion demonstrates a different magnetic behavior. EPR data showed that compound **2** contains about 77% of LS and ~23% of HS Fe(III) centers at  $T_{\text{N}}^{\text{EPR}} = 10.2$  K. It displays a partial spin crossover ( $S = 5/2 \leftrightarrow 1/2$ ) above 150 K and undergoes the antiferromagnetic ordering below 10.2 K. The obtained results and the results of DFT calculations allowed us to conclude that a bilayered packing with a chain structure of Fe(III) centers in ionic bilayers is formed in compound **1**, whereas a dimeric structure of Fe(III) centers is formed in compound **2**. Thus, the ability of the counterion to form an effective network of hydrogen bonds and its size define the packing motif of the  $[\text{Fe}(\text{L})_2]^+$  complexes. Therefore, the replacing of the counterion has a significant impact on the magnetic properties of the compound.

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## 1. Introduction

The spin-crossover (SCO) phenomenon, where spin states may be switched reversibly between low-spin (LS) and high-spin (HS) configurations by external stimuli such as temperature, pressure and more rarely light irradiation, termed the LIESST effect [1–7], can occur in transition metal complexes with a  $d^4$ – $d^7$  electron configuration [1–4]. In particular, the light-induced excited spin-state trapping (LIESST effect), which induces conversion of a LS state to a HS state by means of light irradiation, has attracted considerable

interest. Among the most extensively studied SCO materials are complexes of iron(II) ( $d^6$ ) [8–10] and iron(III) ( $d^5$ ) [11], which have caused the interest of many researchers as potential multifunctional materials in fields such as molecular electronics, memory storage, sensors and photoelectric devices [12–15]. However, such applications require that the spin transition occurs abruptly at ambient temperature (ideally room temperature) and with wide thermal hysteresis (for the memory effect) [16,17].

In the case of iron(III), which has a  $d^5$  electron configuration, the transition occurs from a high spin state ( $^6\text{A}_1$ ,  $S = 5/2$ ) to a low spin state ( $^2\text{T}_2$ ,  $S = 1/2$ ) [18,19]. Iron(III) compounds, compared to the iron(II) systems, have the advantage of generally being air stable and thus would be expected to be more amenable to processing

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